



Review

# Methods for the Treatment of Cattle Manure—A Review

Carolina Font-Palma 

Department of Chemical Engineering, Faculty of Science and Engineering, Thornton Science Park, University of Chester, Chester CH2 4NU, UK; c.fontpalma@chester.ac.uk; Tel.: +44(0)-1244-512377

Received: 28 February 2019; Accepted: 6 May 2019; Published: 15 May 2019



**Abstract:** Environmental concerns, caused by greenhouse gases released to the atmosphere and overrunning of nutrients and pathogens to water bodies, have led to reducing direct spread onto the land of cattle manure. In addition, this practice can be a source of water and air pollution and toxicity to life by the release of undesirable heavy metals. Looking at the current practices, it is evident that most farms separate solids for recycling purposes, store slurries in large lagoons or use anaerobic digestion to produce biogas. The review explores the potential for cattle manure as an energy source due to its relatively large calorific value (HHV of 8.7–18.7 MJ/kg dry basis). This property is beneficial for thermochemical conversion processes, such as gasification and pyrolysis. This study also reviews the potential for upgrading biogas for transportation and heating use. This review discusses current cattle manure management technologies—biological treatment and thermochemical conversion processes—and the diverse physical and chemical properties due to the differences in farm practices.

**Keywords:** cattle manure; beef cattle; gasification; anaerobic digestion; biogas; biomethane

## 1. Introduction

The beef cattle industry represents a viable source of waste biomass produced all year round. In the UK, ten millions of cattle and calves are being grown annually [1]. In the USA, the annual inventory of cattle and calves is of 94 million [2]. Texas, Kansas and Nebraska are the three states with the largest beef cattle production. Other large cattle producers are Brazil with 218 million, India 186 million, China 83 million, Argentina 53 million, and Australia 26 million in 2017 [3].

Feedlot cattle can generate manure about 5–6% of their body weight each day, a dry mass of roughly 5.5 kg per animal per day. Full-grown milking cows can produce 7–8% of their body weight as manure per day, roughly a dry mass of 7.3 kg per animal per day. A dry mass of about 24 billion tonnes of dairy manure is produced per year in the USA [4]. According to the 2010 census, 31.3 million tonnes of dairy and beef cattle manure as undiluted slurry, and 35.7 million tonnes of dairy and beef cattle manure handled as solids were produced in the UK [5].

Cattle manure can end up as slurry, which combines excreta produced by livestock with rainwater and wash water and, in some instances, waste bedding and feed. Slurry and solid manure have traditionally been spread directly onto land as fertilisers [6]. However, these may be potential sources of water and air pollution. Water pollution, by overflowing slurry store or run-off after heavy rain, can affect fish and aquatic life by increased biochemical oxygen demand (BOD), dissolved ammonia, and phosphorous presence causing algal blooms in freshwater systems. Air pollution is attributed to ammonia gas released into the atmosphere from manures spread on the land and stored in livestock buildings. In the UK, 115.8 kt come from cattle which is one of the largest sources representing 41% of all UK ammonia emissions in 2017 [7]. Health issues have been raised by studies for the characterisation from manure application which have revealed that mercury (Hg), copper (Cu) and zinc (Zn), pose a

high risk to humans and the environment in Europe as well as South-East Asia [8]. These findings are useful to guide policy-making to set specific targets for heavy metals contained in feedstuff and animal manure.

Another challenge with livestock manure management is the extensive use of water. Dairy farms use approximately 435 L of water per cow per day (about 113 L for drinking and the rest for flushing manure alleys) [9]. This estimation does not take into account the water required for milking, cleaning, and irrigating the crops that feed the livestock.

Feedlot manure varies due to differences in climate, type of feedlot surface, and management practices. Cattle manure is a good source of nutrients, such as nitrogen (N), phosphorus (P), potassium (K), sulfur (S), and magnesium (Mg) coming from livestock diets, as well as other trace elements. Reported values of nutrients found in cattle manure include 7.89 g kg<sup>-1</sup> for P, 38.45 g kg<sup>-1</sup> for K [10], and 2–8.1 g kg<sup>-1</sup> for N [11]. Table 1 shows alkali composition from manure ashes. As a result, raw cattle manure or composted manure applied to agricultural land can help increase crop productivity and soil fertility for a longer term than synthetic fertilisers since synthetic fertilisers have higher energy requirements, they pose nitrate leaching potential, and are unable to improve N and C soil nutrient levels over time [12]. A study carried out for ten years found that the mean corn grain yield when cattle manure and swine effluent were applied were about double and 1.8 times greater than the untreated control, respectively [13]. However, manure may contain traces of antibiotics, heavy metals and pathogens, which pose a threat to ecosystems and humans [14]. These toxic constituents not only affect the plants by salt toxicity through direct application, but also the grazing cattle and humans via the food chain of accumulated toxins [8].

Proper manure management practices must be in place to minimise environmental impacts. UK greenhouse gas emissions (GHG) were reported as 42 MtCO<sub>2</sub>e coming from the agriculture sector in 2016 [15]. These emissions represent 10% of the total UK GHGs, which include emissions of mostly methane (62%) due to enteric fermentation from cattle, nitrous oxide (35%) because of fertilisers used on soils and CO<sub>2</sub> (3%) [16]. UK agricultural emissions decreased by 16% in 2016 compared to those in 1990, which is attributable to a fall in livestock numbers and a reduction in the use of synthetic fertiliser. GHG emissions reduction has concentrated more recently on reducing CO<sub>2</sub> emissions. However, methane poses a higher global warming potential (GWP) for methane is 84 for a lifetime of 20 years and 28% for 100 years relative to CO<sub>2</sub> [17] since it has a higher radiative energy impact but over a shorter atmospheric lifetime than CO<sub>2</sub>.

High worldwide population and the increasing demand for food have favoured cattle production operations, where the selection of proper manure disposal methods needs to be addressed. As a response to this big waste challenge, different waste management options have been explored to replace the traditional spread of manure onto soils. Therefore, this work discusses biochemical and thermochemical processes, current operating practices to reduce solids whilst producing energy, and explores its potential to upgrade biogas for transportation and heating usage.

## 2. Characteristics of Cattle Manure

In order to dispose properly and/or utilise cattle manure, this waste stream needs to be characterised to evaluate its value as feedstock, e.g., C/N, elemental composition, heavy metal content, and GHG emissions. Numerous reports have presented the physical and chemical properties of cattle manure, as described below.

### 2.1. Moisture Content

The moisture content reported is not very consistent among different sources. Table 2 shows values ranging from 13 to 75 wt %. The upper values will have significant implications in thermochemical conversion processes, since energy will be needed to dry the material.

## 2.2. Ash Content

With the high ash content found in cattle manure (10.8–45.2 wt % dry basis), compared to wheat straw (4.7–10.3 wt % db), ash-related problems could emerge—including sintering, agglomeration, deposition, erosion and corrosion—due to the low melting point of ash in manure feedstocks. A detailed evaluation of a wide range of temperatures is recommended to assess ash effects during manure gasification. The ash content and composition depend on the type of bedding used.

In the USA, dairies use fine and coarse sand, straw, sawdust, composted manure, and shredded newspaper [18]. The most recommended bedding material is sand because sand bedding promotes a dry and clean environment, prevents bacterial growth and provides cows with a comfortable space to lie on. Under the bedding, a stall base is used to keep cleanliness and prevent hock injuries. The most common materials used as stall base are concrete, rubber mat, mattress, waterbed and dirt. Table 2 shows the properties of dairy manure when sand is used as bedding material, which prompts high ash content.

**Table 1.** Ash composition of manure, alkali index and melting behaviour.

Ash Composition (wt % of Ash)	Beef Cattle Manure [19] <sup>a</sup>	Dairy Cattle Manure [19] <sup>b</sup>	Cattle Manure [20]
P <sub>2</sub> O <sub>5</sub>	7.19	19.13	3.0
K <sub>2</sub> O	7.02	4.79	6.40
Na <sub>2</sub> O	2.29	1.44	2.0
CaO	7.95	8.90	13.90
MgO	5.42	6.24	3.70
Fe <sub>2</sub> O <sub>3</sub>	1.89	2.03	1.70
CuO	0.04	0.04	-
ZnO	0.08	0.04	-
SO <sub>3</sub>	-	-	2.80
SiO <sub>2</sub>	-	-	53.50
Alkali index (kg alkali/GJ)	1.34	1.18	-
Initial deformation temperature (°C) <sup>c</sup>			1232
Softening or spherical temperature (°C) <sup>c</sup>			1271

<sup>a</sup> 139 beef manure samples from China, <sup>b</sup> 217 dairy manure samples from China, <sup>c</sup> American standard method measured in reducing conditions.

In the UK, straw is mostly used as bedding material. Farm Practices Surveys (FPS2016) guidelines recommend an average mean of straw used of 1.41 tonnes/cow/winter for dairy cattle and 0.32 tonnes/cow/winter for slurry systems. For beef cattle, straw is used on average as 1.01–1.32 t/animal/winter [5].

Carlin et al. [4] reported the properties for low- and high-ash biomass. The differences observed derive from diverse manure management practices. Low-ash manure comes from cement-paved lots. Unfortunately, the majority of the manure is scraped from unpaved feed yards, which contain high amounts of ash. Recycled solids that were screened mechanically from flushing systems are normally of low ash content if sand was not the bedding material.

The sulfur content was reported as high as 1.36 wt % (daf). High sulfur content is undesirable because sulfur in the organic form may generate SO<sub>x</sub> emissions during thermochemical conversion and the emitted SO<sub>x</sub> may contribute to acid rain.

High concentration of alkali metals is associated with low melting temperatures, which are undesirable during thermochemical conversion. Table 1 shows the ash composition from two sources, which show similar concentrations despite the different manure handling conditions and lack of details on bedding material used. The alkali index (AI) has been used as an indicator for fouling and slagging. AI expresses the quantity of alkali oxide in the fuel per unit of fuel energy (kg alkali/GJ) and is defined as  $AI = \text{kg} (K_2O + Na_2O)/HHV$ , where HHV is the higher heating value. For fuels with AI values exceeding 0.34, fouling and slagging problems should be expected [19]. Ashes with high levels of macro- and micro-nutrients have the potential for soil amendment as fertiliser.

**Table 2.** Properties of cattle manure (wt %).

Property	Fresh Cattle Manure [21]	Feedlot Manure [22]	Beef Cattle Manure [19] <sup>a</sup>	Beef Cattle Manure [23]	Cattle/Cow Manure [20] <sup>b</sup>	Dairy Cattle Manure (Sand Bedding) [24]	Feedlot Manure (Low Ash) [4]	Feedlot Manure (High Ash) [4]
Moisture (wt %)	70.7	40.2 ± 1.0	75.66 ± 7.8	13.08 ± 0.5	39.24 ± 35.3			
Ash (wt %)								
Wet basis	10.9	21.5 ± 0.4						
Dry basis	37.2	35.9 ± 0.1	22.64 ± 11.9	29.80 ± 2.8	27.72 ± 17.9	48.8 ± 3.1	13.58	45.23
Heating value (MJ/kg)								
Wet basis	3.9	8.01 ± 0.2						
Dry basis	13.3	13.5 ± 0.5	15.21	15.93 ± 0.3		8.7 ± 1.6	18.65	11.24
Dry (af)	21.2				20.08 ± 0.53		21.58	20.53
Volatiles (wt %)								
Wet basis	15.2							
Dry basis	52	50.2 ± 0.9	64.58 ± 8.1	59.05 ± 0.4		49.1 ± 2.9		
Dry (af)	82.8				83.91 ± 8			
Fixed carbon (wt %)								
Dry basis				11.15 ± 2.9		2.2 ± 0.8		
Dry (af)					16.09 ± 8			
Elemental analysis (% dry and ash-free basis)								
C	49.38	49.66	48.66	50.43	45.54 ± 11.5	32.42	57.43	59.06
H	6.46	5.62	6.80	7.18	6.31 ± 0.14	4.43	6.82	7.03
O	39.79	39.09	41.24	39.29	38.25 ± 3.22	60.55	31.26	28.91
N	3.33	4.28	2.79	2.55	2.2 ± 1.23	2.15	3.88	4.22
S	1.05	1.36	0.76	0.57	0.58 ± 0.41	0.45	0.62	0.78
Chemical formula	CH <sub>1.559</sub> O <sub>0.605</sub> N <sub>0.058</sub> S <sub>0.008</sub>		CH <sub>1.684</sub> O <sub>0.639</sub> N <sub>0.05</sub> S <sub>0.006</sub>					

<sup>a</sup> 139 beef manure samples from China, <sup>b</sup> Average values of four samples of cattle/cow manure, af: ash-free basis.

For health and welfare purposes, some heavy metals are added to animal feeds, for example, copper is as an additive to improve the hoof quality of dairy cows, and a large portion of those heavy metals consumed end up in manure [14]. Table 3 reports heavy metal concentrations in cattle manure collected as solid (manure collected from floors with bedding) and as a liquid slurry (manure washed out of enclosed areas). Of particular concern are those heavy metals that can cause health problems when entering the human chain, such as cadmium (Cd), lead (Pb) and Hg. Increased trace elements in soil transfer into plants, for example plants grown on soils with Cu contents of 32–640 mg/kg DM accumulate 8.1–82.6 mg Cu/kg DM in plant tissue, making them potentially inappropriate for animal and human consumption (upper limits of Cu content in cattle feed: 15 mg/kg) [25]. Difference between dairy and beef cattle manure is due to mineral supplements added to feed. An inventory on beef cattle feeds reported concentrations ranging from 22 to 777 mg/kg dm (dry matter) for Zn, 3.7–61.5 mg/kg dm for Cu, <1–4.99 mg/kg dm for Pb and <0.1–0.79 mg/kg dm for Cd [26]. Table 3 shows the limits set by different countries for heavy metal content in compost. Slurries tend to have higher heavy metal concentrations, with Cd, Cu and Zn concentrations outside the compost limits in some instances.

**Table 3.** Heavy metal contents in manure against standard limits in compost (mg/kg dry matter).

	Limits in Compost					
	UK (BS EN 13650) [27]	USA [28]	China [28]	Dairy Cattle Manure [26]	Dairy Cattle Slurry [26]	Beef Cattle Manure [26]
<b>As</b>	–	41	15	0.57–4.83	<0.1–4.48	0.39–1.53
<b>Cd</b>	1.5	39	3	<0.1–0.53	<0.1–1.74	<0.1–0.24
<b>Cr</b>	100	–	150	0.77–21.40	<0.2–12.9	0.79–2.05
<b>Cu</b>	200	1500	–	26.2–55.8	<1.0–352	10.5–27.9
<b>Ni</b>	50	420	–	1.7–9.1	0.1–11.4	0.2–3.1
<b>Pb</b>	200	300	50	<1.0–9.18	<1.0–16.9	<1.0–6.4
<b>Zn</b>	400	2800	–	99–238	<5–727	41–274

### 2.3. Volatiles

On dry and ash-free basis (daf), the compositions for the elemental analysis of cattle manure are consistent (see Table 2) with a carbon content of up to 50 wt %.

Cattle manure presents high levels of volatile matter (50.2–64.6 wt % dry basis), which is highly beneficial for gasification.

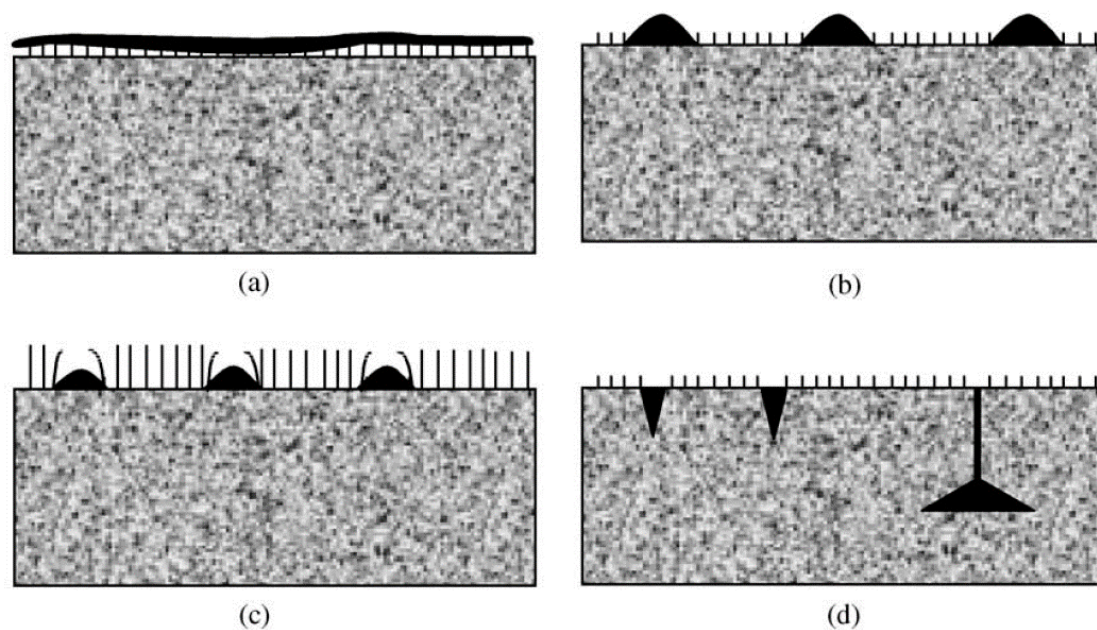
### 2.4. Energy Content

The heating value of cattle manure is of around 13.5 MJ/kg (dry basis), which is about half of the value for coal (16–24 MJ/kg for sub-bituminous).

## 3. Current Waste Management/Disposal Practices

Based on recent surveys, farmyard manures are stored in concrete floor compounds (40%) and temporary field heaps (60%) in England. In the UK, a larger share of cattle slurry manures is applied to grassland in spring than to tillage in autumn [5]. In order to minimise ammonia emissions, low emission spreading techniques (LEST) are recommended, such as trailing hose, trailing shoe applicator, and shallow injection. These techniques can be mounted to a vacuum or pumped tanker [29]. Figure 1 shows a schematic of these slurry application techniques. Despite the potential of LESTs for the reduction in NH<sub>3</sub> loss of 40–90% compared to surface broadcast applications, surface broadcast techniques dominate the slurry application in the UK mainly due to cost [5].





**Figure 1.** Schematic representation of slurry application by (a) surface broadcast, (b) trailing hose, (c) trailing shoe, and (d) shallow or deep injection. Reproduced with permission from [29]. Copyright Elsevier, 2002.

Manure has been used to produce recycled manure solids (RMS)—often called ‘green bedding’—for use as bedding material for dairy cows over the last years, and this practice is increasing in the UK [30]. The Bauer FAN screw press separator is the common equipment used to produce RMS bedding in the UK. Farmers are opting for RMS as bedding because of its cost, benefits on cow comfort and cleanliness, difficulties with the supply of alternative bedding materials, ease of slurry storage and handling, reduced dust and ease of bedding handling. The EU Animal By-Products (ABP) Regulation (EU Reg. 1069/2009) has provisions that permit the use of RMS, as long as this does not pose risks to human or animal health [31]. Composting is also commonly used for the disposal of animal manure to produce a stabilised fertiliser that is spread onto land with no or little odour, pathogens and nitrates. However, C and N losses decrease the value of the compost as fertiliser, and those losses contribute to greenhouse gas emissions [32].

In the UK, 77% of dairy farms have a nutrient management plan in place for their holdings, and only 2.6% of farmers reported to process slurries by anaerobic digestion in 2016 [1]. In North America, storage of millions of litres of manure in enormous lagoons is the most common manure management practice [9]. These lagoons are on average 4.5 m deep (2.4 to 6 m) with surface areas ranging from 2000 to 8000 m<sup>2</sup> [33].

Separators and bedding systems are also used for manure management. Their main purpose is to separate solids for recycling purposes. For example, the solids can be used for bedding or composting. However, the overall volume remains the same and odour is not removed [9]. There are machines designed to separate fibres or sand when used as bedding for cows from manure. Sand can be recovered and reutilised.

Table 4 shows a summary of current commercial solutions. These practices include mechanical separation or biological treatment, where thermochemical conversion processes do not seem yet to have found commercial exploitation using cattle manure as feedstock.

**Table 4.** Commercial technologies to treat slurries and manure from cattle operation.

Technology	Company	Features
Bioremediation of dairy wastewater	BIOWiSH Technologies [34]	Biocatalyst can be added directly or mixed with water to the lagoon inflow. The process results in a significant reduction of biochemical oxygen demand (BOD), and total suspended solids (TSS) by almost 50%
Mechanical (membranes) and chemical treatments	Livestock Water Recycling [35]	The process extracts up to 75% of water from manure. By concentrating and segregating the nutrients, it results in clean, potable water, dry solids that are rich in both phosphorus and organic nitrogen and concentrated stable ammonium and potassium liquid.
Windrow Composting method	Allance Fertiliser Machinery [36]	Process up to 50,000 ton/year. Waste is dumped on ground to form piles of 1.5–2.5 m height. The process takes 4–6 weeks. In the first two weeks, turning is required every two to three days when the temperature is 55 °C or above. Finally, the compost is dried, ground to produce a finer material, and screened to remove larger particles (e.g., fractions >10 mm will be discarded).
Recycled manure solids (RMS)	DariTech [37]	There are composter options for up to 1400 cows. Dewatered flush manure is first fed into a separator to deliver solids with 35% (dry matter) of manure solids. Then the solids are composted using bacteria within and then air is supplied.
Separators and bedding systems	Sand-Manure Separators (SMS), McLanahan [38]	80 to 90% of sand can be captured, which can be recycled as bedding. It also processes a nearly sand-free manure effluent.
Separators	GEA [39]	Process daily manure output of up to 300 cows per hour. The process allows to recover liquid and fibres contained in manure in order to produce compost or bedding
Anaerobic digestion	HoST bio-energy installations [40]	The process consists of a digester integrated with combined heat and power (CHP). There are two versions: one capable of producing 65–150 kWe and the other 200–400 kWe
Anaerobic digestion	Dairy Energy [41]	It requires 1500 m <sup>3</sup> of liquid manure per annum and 200 of space. It has a capacity of 11–44 kW using a CHP system.

#### 4. Advanced Options for the Treatment/Conversion of Cattle Manure

##### 4.1. Biological Treatment

###### 4.1.1. Composting and Vermicompost

Stabilisation is a technique widely used to eliminate hazards through the reduction of microbial activity and content of labile compounds, which makes manure safer and stabilised for soil application as fertiliser [42]. There are two main methods for biological stabilisation: composting and vermicomposting.

Composting consists of accelerating bio-oxidation of organic matter using microorganisms under controlled conditions. The process involves a thermophilic stage with the release of heat, CO<sub>2</sub> and water. The resultant stabilised material is odourless with reduced volume and weight, which eases its handling and storage [43]. The disadvantage of composing is the nutrient loss, where nitrogen is lost

(up to 40% of total N) through ammonia volatilisation. Not only nutrients are lost decreasing the value of compost as fertiliser, but also those losses contribute to GHG emissions [32].

Vermicomposting is also a process relating to the bio-oxidation and stabilisation of organic material, but by both microorganisms and earthworms. The former are responsible for the biochemical degradation of the organic matter, and the latter of driving the process because earthworms aerate, prepare and fragment the substrate for microbial activity. Microbial activity and further decomposition are favoured by physical and chemical modification (e.g., reduction of C:N ratio) and an increase of surface area for microorganisms by the mechanical blending and breaking down of organic matter by earthworms [44]. However, it is recommended that heavy metal concentration should be kept at low levels to avoid the transfer of bioavailable metals from earthworms into the food chain [45].

Table 5 compares the chemical changes of treated manure by different biological processes, including composting followed by vermicomposting. Higher decomposition was observed for vermicomposting and the combined treatment, since the C to N ratio decreases as N is lost at a lower rate than carbon as CO<sub>2</sub> [42]. Mineral N (NH<sub>4</sub><sup>+</sup> and NO<sub>3</sub><sup>-</sup>) increased after the three stabilisation methods, which shows a significant level of mineralisation.

**Table 5.** Physicochemical and biochemical properties of raw cattle manure and substrates produced by different treatments: incubation under field conditions for 15 days (control), active phase of composting (composting), vermicomposting, and composting with subsequent vermicomposting (composting + vermicomposting) [42].

	Raw Cattle Manure (Straw as Bedding)	Control	Composting	Vermicomposting	Composting + Vermi-Composting
pH	7.70–8.94	8.89–8.78 <sup>a</sup>	8.86–8.07 <sup>a</sup>	7.73–7.51 <sup>b</sup>	7.85–7.14 <sup>b</sup>
EC (dS m <sup>-1</sup> )	1.25 ± 0.08	1.32 ± 0.08 <sup>a</sup>	2.13 ± 10 <sup>b</sup>	0.78 ± 0.02 <sup>c</sup>	0.72 ± 0.04 <sup>c</sup>
C to N ratio	17.0 ± 0.74	15.7 ± 1.09 <sup>a</sup>	17.5 ± 0.33 <sup>a</sup>	11.1 ± 0.24 <sup>b</sup>	11.3 ± 0.16 <sup>b</sup>
Total C (g kg <sup>-1</sup> dw)	399.2 ± 2.8	395.7 ± 3.2 <sup>a</sup>	384.9 ± 2.7 <sup>a</sup>	314.0 ± 5.4 <sup>b</sup>	309.0 ± 8.6 <sup>b</sup>
Total N (g kg <sup>-1</sup> dw)	23.6 ± 0.9	25.6 ± 1.7 <sup>ab</sup>	22.0 ± 0.3 <sup>a</sup>	28.3 ± 0.2 <sup>b</sup>	27.4 ± 0.8 <sup>b</sup>
DON (mg kg <sup>-1</sup> dw)	2190 ± 380	2260 ± 244 <sup>a</sup>	2571 ± 896 <sup>a</sup>	3726 ± 153 <sup>a</sup>	2165 ± 198 <sup>a</sup>
NH <sub>4</sub> -N (mg kg <sup>-1</sup> dw)	610 ± 92	534 ± 128 <sup>a</sup>	1235 ± 291 <sup>b</sup>	276 ± 24 <sup>a</sup>	191 ± 30 <sup>a</sup>
NO <sub>3</sub> -N (mg kg <sup>-1</sup> dw)	19 ± 15	0 ± 0 <sup>a</sup>	721 ± 184 <sup>b</sup>	917 ± 113 <sup>b</sup>	829 ± 110 <sup>b</sup>
DOC (mg kg <sup>-1</sup> dw)	4406 ± 704	6819 ± 772 <sup>a</sup>	9338 ± 2103 <sup>a</sup>	5249 ± 302 <sup>a</sup>	4825 ± 387 <sup>a</sup>
Available P (mg kg <sup>-1</sup> dw)	211 ± 6	175 ± 7 <sup>a</sup>	342 ± 22 <sup>b</sup>	111 ± 3 <sup>c</sup>	109 ± 6 <sup>c</sup>

DON: Dissolved organic nitrogen, DOC: Dissolved organic carbon, EC: Electrical conductivity dw: Dry weight, a,b,c: Means with the same letter were not statistically different (Tukey HSD test,  $\alpha = 0.05$ ).

#### 4.1.2. Anaerobic Digestion

Anaerobic digestion is mostly popular in Europe for manure management. The benefits are that biogas is produced and can be used for electricity generation. The typical biogas consists of 53–70% of CH<sub>4</sub> and 30–47% of CO<sub>2</sub> and other impurities, if upgraded by removing CO<sub>2</sub> it can be injected directly into the natural gas grid [46], and this is addressed in Section 5.3. The liquid digestate produced is commonly spread on crops, however, it lacks nutrient content [9]. Different solutions are available to accelerate sludge decomposition and reduce odours.

Anaerobic digestion (AD) is a biochemical process where several groups of microorganisms degrade organic matter into a gaseous mixture consisting mainly of methane and carbon dioxide called ‘biogas’ and a digestate, in an oxygen-free environment. AD represents an attractive technology for the management of animal manure due to twofold reasons: the associated methane emission to the atmosphere is reduced, and the biogas produced becomes a renewable energy source [47]. AD consists of four stages [48]:

- (1). Hydrolysis: In this step, extracellular enzymes transform complex, undissolved material (carbohydrates, proteins and fats) into their respective monomers (sugars, amino acids, lipids), which are taken by the microorganisms for further degradation;



- (2). Acidogenesis: In this step, the dissolved compounds present in cells of fermentative bacteria convert simple monomers into volatile fatty acids (VFAs), alcohols, lactic acid, CO<sub>2</sub>, H<sub>2</sub>, NH<sub>3</sub> and H<sub>2</sub>S, as well as new cell material;
- (3). Acetogenesis (intermediary acid production): In this step, digestion products (higher volatile fatty acids) are transformed into acetate, H<sub>2</sub> and CO<sub>2</sub>, as well as new cell material;
- (4). Methanogenesis: In this stage, acetate, hydrogen plus carbonate, formate or methanol are converted into methane, CO<sub>2</sub> and new cell material.

Anaerobic digestion is affected by the pH, temperature, nature of the feedstock (e.g., composition and nutrients), presence of toxic or inhibitory substances and organic loading rate [49]. AD also requires carbon and nitrogen for microorganisms to grow. There is no consensus for optimum value for C/N ratio, but it has been reported that value in the range of 15–30 is needed for biogas production [50]. Higher C/N ratios limit microbial growth due to nitrogen shortage which leads to a lower methane yield due to deactivation of methanogens and possible process failure. In contrast, lower C/N ratios limit the microbial growth due to carbon deficiency, which can lead to an increase in ammonia nitrogen and volatile fatty acids (VFA) in the digester.

Animal manures contain high nitrogen levels that deviate for an optimum C/N ratio required for anaerobic digestion. As a result, anaerobic digestion of only animal manure delivers a low methane yield. Neshat et al. [51] have reviewed how to increase the carbon content of animal manure before the anaerobic digestion process. They proposed lignocellulosic materials such as agricultural wastes as potential candidates to compensate for the carbon deficit of animal manure.

The slow degradation of lignocellulosic sources solely, and as a result, low methane yield, limits their use for anaerobic digestion. The slow hydrolysis of cellulose controls the digestibility rate of lignocellulose materials, as a rate—controlling step of the process. Co-digestion of animal manures and lignocellulosic feedstocks have been proposed as a solution to match the C/N ratio needed as an optimum value for anaerobic digestion to produce biogas and a nutrient-rich residue that can be employed as fertiliser. Co-digestion of animal manures with lignocellulosic materials permits the dilution of toxic compounds, usage of nutrients, and reduction of the risk of ammonia inhibition [51]. Wheat straw, second abundant agricultural waste in the world, has a C/N ratio of 81, which is too high for anaerobic digestion [21]. Experiments for the co-digestion of dairy manure and wheat straw with C/N ratios of 25 and 30 exhibited better digestion performances, due to stable pH and low concentrations of total ammonium nitrogen and free NH<sub>3</sub>. Cow manure has been reported with a low C/N ratio of 11–14 [52]. To balance this ratio, 30–40% crops were added to cow manure, which increased the C/N ratio of 15–25 for the mixture closer to the optimum values for co-digestion.

Cattle manure has also been co-digested with milk thistle (*Silybum marianum*), which delivers a high biomass yield, is flexible to different cultivating conditions, and grows well under water shortfalls. The biomass yield of milk thistle grown under semiarid Mediterranean climate conditions is around 20 t ha<sup>-1</sup>. Milk thistle is mostly grown for its seeds, which are beneficial to cure human liver diseases and maintain animal wellbeing. The residue from its cultivation has been proposed as a substitute of maize for methane production [53]. Milk thistle crop in a naturally sun-dried form was evaluated after mechanical, thermal and thermo-chemical pre-treatments. Pre-treatment with NaOH increased the solubilisation by 77.7% and delivered a methane yield of 271 L CH<sub>4</sub> kg<sup>-1</sup> of volatile solids by co-digestion with cattle manure.

Xavier et al. [47] compared the performance of particle size reduction of wheat straw when co-digested with cattle manure. Particle size reduction accelerates the hydrolysis and acidogenesis stages of AD, causing a faster and higher methane yield. Two methods were compared—shredding and briquetting. Briquetting is a mechanical process, where biomass is first shredded and then subjected to high pressure promoting its densification and resulting in briquettes with a density of around 1.2 kg L<sup>-1</sup>. Co-digestion of shredded or briquetted wheat straw with cattle manure increased total solids (TS) and volatile solids (VS) concentration due to increased cellulose and hemicellulose concentrations. The mixture of cattle manure and briquetted wheat straw delivered a 33% higher

specific methane yield compared to cattle manure alone ( $263 \text{ L}_{\text{STP,CH}_4} \text{ kg}^{-1} \text{ VS}$ ) and 158% of volumetric methane yield. The net energy yields were the same for both techniques for particle size reduction. However, the briquetting technology could reduce handling and transportation costs when transported over longer distances.

In addition to anaerobic digestion of livestock slurries, recycling of nutrients and water from digestate has been proposed to grow algal biomass (*Scenedesmus* sp.) [54]. The digestate has improved fertilising properties after protein degradation and ammonia accumulation. Thus, a farm-level integrated process will consist of cattle manure treatment with biogas production, recycling of nutrients and water from digestate treatment, and the production of algal biomass consuming the nutrients from liquid streams. This integration could facilitate farms with an increase in agricultural incomes to invest in an expensive AD technology.

#### 4.2. Thermochemical Conversion

Thermochemical conversion processes include combustion, gasification, and pyrolysis. These processes have the advantage of short residence times (hours compared to days or weeks needed in biological treatment).

##### 4.2.1. Pyrolysis

Pyrolysis occurs in the absence of oxygen, and is also the first step to combustion and gasification. When selecting a lower reaction temperature, slow heating rate and long residence time, pyrolysis produces mainly biochar. Studies have shown that the application of biochar from cow manure to sandy soil as beneficial for maize growth, and as well as for the improvement of the physicochemical properties of the coarse soil [55]. Physical, chemical and mineralogical properties were tested in biochars produced from dairy manure at various low temperatures ( $100\text{--}500^\circ\text{C}$ ), where pH, ash content and surface area increased with temperature rise [56]. The biochar showed considerable capability for adsorption for Pb and atrazine from aqueous solution when the dairy manure was treated at  $<200^\circ\text{C}$ , which has the potential as an effective adsorbent for environmental remediation. In contrast, fast pyrolysis produces a higher amount of bio-oil. For the fast pyrolysis of swine manure in a bubbling-fluidised-bed reactor, it was found that the highest bio-oil yield was of 18.48 wt % at  $600^\circ\text{C}$  [57].

The kinetic and thermodynamic behaviour of cattle manure under pyrolysis conditions has been studied to better understand the decomposition stages (as shown in Table 6). The pyrolysis process is composed of three stages: Stage I denotes the reaction zone of the extractives and hemicellulose component, stage II derives from cellulose and lignin components, and stage III corresponds to lignin and mineral components. This information is useful for the design of pyrolysers. The apparent activation energy,  $E$ , was calculated using various isoconversional methods and degree of conversion ( $\alpha$ ) [58],

$$\alpha = \frac{w_0 - w_t}{w_0 - w_\infty} \quad (1)$$

where  $w_0$  is the initial sample weight  $w_t$  is the sample weight at time  $t$ , and  $w_\infty$  is the final sample weight.

**Table 6.** Kinetic characteristics of pyrolysis stages [58].

	Stage I	Stage II	Stage III
<b>Conversion degree (<math>\alpha</math>)</b>	0.05–0.35	0.35–0.55	0.55–0.85
<b>Apparent activation energy (<math>E</math>, <math>\text{kJ mol}^{-1}</math>)</b>	$149.62 \pm 19.95$	$172.81 \pm 3.25$	$262.16 \pm 86.10$
<b>Decomposition temperature (<math>^\circ\text{C}</math>)</b>	105–300	300–330	330–800

##### 4.2.2. Gasification

Gasification aims to produce a usable flue gas, often called syngas, which comprises mostly carbon monoxide, carbon dioxide, and hydrogen (see Table 7). The produced syngas can be used

directly as fuel for heating or in gas turbines and engines, or utilised as feedstock to produce chemicals such as methanol, or if upgraded by removing CO<sub>2</sub> for the production of hydrogen. In gasification, the syngas is produced by burning the fuel or biomass under an oxygen environment lower than the stoichiometric oxygen required for complete combustion [59]. Therefore, the equivalence ratio (ER) concept is widely used in energy conversion processes, especially during gasification. ER is the ratio of fed air to the stoichiometric air for complete combustion. Its determination is straightforward for fuels of known chemical formula, e.g., ethanol. However, for biomass, the determination of the stoichiometric ratio (SR) of air to fuel for complete combustion is more complex. SR can be calculated from the elemental composition of the fuel [60]:

$$SR = \left( \frac{C_C}{12} + \frac{C_H}{4} - \frac{C_O}{32} \right) \left( 1 + \frac{79}{21} \right) \left( 1 - \frac{C_A}{100} \right) \frac{28.84}{100} \quad (2)$$

where  $C_C$ ,  $C_H$ , and  $C_O$  represent the weight content of carbon, hydrogen and oxygen on an ash-free basis, and  $C_A$  is the ash content, or by using a correlation between HHV and SR:

$$SR = 0.31HHV \quad (3)$$

Then, the equivalence ratio (ER) is calculated using the actual air to fuel ratio divided by SR [60].

In order to assess gasification performance, its efficiency is reported under different criteria:

Cold gasification efficiency ( $\eta_G$ ) describes the ratio of the heat content of the fuel gas generated during the process of gasification at ambient conditions and of the heat content of biomass (e.g., cattle manure) when entirely burnt, using Equation (4) [61].

$$\eta_G = \frac{\dot{V}_g LHV_g}{\dot{m}_b LHV_b} \quad (4)$$

where  $\dot{V}$  is the volumetric flowrate,  $\dot{m}$  is the mass flow rate,  $LHV_g$  is the lower heating value of the syngas in MJ/Nm<sup>3</sup>, and  $LHV_b$  is the lower heating value of biomass in MJ/kg.

The energy conversion efficiency of gasification is calculated using Equation (5) as follows:

$$\eta_E = \frac{S_y \text{ HHV}_{\text{gases}}}{\text{HHV}_b} \times 100\% \quad (5)$$

where,

$$\text{HHV}_{\text{gases}} = V_{\text{CO}} \text{HHV}_{\text{CO}} + V_{\text{CO}_2} \text{HHV}_{\text{CO}_2} + V_{\text{CH}_4} \text{HHV}_{\text{CH}_4} + V_{\text{N}_2} \text{HHV}_{\text{N}_2} + V_{\text{H}_2\text{O}} \text{HHV}_{\text{H}_2\text{O}} + V_{\text{H}_2} \text{HHV}_{\text{H}_2} \quad (6)$$

$\eta_E$  (%) is the energy gasification efficiency,  $S_y$  (Nm<sup>3</sup>/kg) is the syngas yield obtained by gasification per kg,  $V_{\text{CO}}$ ,  $V_{\text{CO}_2}$ ,  $V_{\text{CH}_4}$ ,  $V_{\text{H}_2}$ ,  $V_{\text{H}_2\text{O}}$  and  $V_{\text{H}}$  are the volume fractions of the syngas obtained by gasification. The heating values of the gas components are  $\text{HHV}_{\text{CO}} = 12.68$  MJ/Nm<sup>3</sup>,  $\text{HHV}_{\text{CO}_2} = 0$  MJ/Nm<sup>3</sup>,  $\text{HHV}_{\text{CH}_4} = 39.78$  MJ/Nm<sup>3</sup>,  $\text{HHV}_{\text{H}_2} = 12.81$  MJ/Nm<sup>3</sup>,  $\text{HHV}_{\text{H}_2\text{O}} = 2.01$  MJ/Nm<sup>3</sup> and  $\text{HHV}_{\text{N}_2} = 0$  MJ/Nm<sup>3</sup>, and  $\text{HHV}_b$  (MJ/kg) is the thermal energy of biomass per kg [19].

For mixtures of air and steam used as oxidiser, the energy conversion efficiency is estimated by [62]:

$$\eta_E = \frac{S_y \text{ HHV}_{\text{gases}}}{\text{HHV}_b + (\lambda + 4.18(T - 298))} \times 100\% \quad (7)$$

where,  $\lambda$  is the latent heat of steam or enthalpy of vaporisation.

Carbon conversion efficiency ( $\eta_c$ ) refers to

$$\eta_c = \frac{V_g \times 1000 [V_{\text{CH}_4}\% + V_{\text{CO}}\% + V_{\text{CO}_2}\% + 2(V_{\text{C}_2\text{H}_2}\% + V_{\text{C}_2\text{H}_6}\% + V_{\text{C}_2\text{H}_4}\%)] \times 12/22.4}{W(1 - X_{\text{ash}}) \times C\%} \times 100\% \quad (8)$$

where  $V\%$  are the gas concentrations in %vol.,  $V_g$  ( $\text{N m}^3/\text{h}$ ) is the dry product gas flow rate,  $W$  is the dry biomass feeding rate ( $\text{g/h}$ ),  $X_{\text{ash}}$  is the ash content in the feed, and  $C\%$  is the carbon content in the ultimate analysis of biomass [63].

**Table 7.** Synthesis gas production.

	Beef Cattle Manure ( $T = 730^\circ\text{C}$ , ER = 0.35) [23]	Pine Wood ( $T = 780\text{--}830^\circ\text{C}$ , ER = 0.18–0.45) [64]	Dairy Biomass ( $T = 519\text{--}1015^\circ\text{C}$ , ER = 0.16–0.63, S/F = 0.4–0.8) [65]	Beef Cattle Manure (Equilibrium Conditions: $T = 850^\circ\text{C}$ , ER = 0.3) [19]
<b>Synthesis Gas Composition (%vol)</b>				
Hydrogen	$7.72 \pm 0.26$	5.0–16.3	13.48–25.45	19.12
Carbon monoxide	$10.92 \pm 0.23$	9.9–22.4	4.77–11.73	19.21
Carbon dioxide	$14.18 \pm 0.43$	9.0–19.4	11–25.2	8.25
Methane	$4.38 \pm 0.13$	2.2–6.2	0.43–1.73	0.64
Ethane	$0.43 \pm 0.02$	0.2–3.3 <sup>a</sup>	0.20–0.69	
Nitrogen	$56.67 \pm 1.33$	41.6–61.6		45.03
Water				7.75
LHV ( $\text{MJ Nm}^{-3}$ )	4.19	3.7–8.4		
HHV ( $\text{MJ Nm}^{-3}$ )			3.27–4.28	5.14
Gas yield ( $\text{Nm}^3 \text{ kg}^{-1}$ biomass)	1.87	1.25–2.45		2.16
Carbon conversion efficiency (%)	90.45			
Cold Gasification efficiency (%), $\eta_G$	49.19			
Energy conversion efficiency (%)			24–69	72.36
<b>Biochar Proximate Analysis (db) (%wt)</b>				
Volatile matter	16.2			
Ash	81.18			
Fixed carbon	2.62			

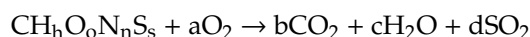
S/F: steam to fuel ratio, <sup>a</sup>  $\text{C}_2\text{H}_n$ , ER equivalence ratio.

Pilot-scale studies using beef cattle manure are found in the literature. Beef cattle manure was tested during air-fired gasification using a bubbling fluidised bed gasifier. Experiments were conducted using an ER ratio of 0.35 at  $730^\circ\text{C}$  in order to minimise the potential for fouling, slagging and/or agglomeration. The stoichiometric air to fuel was estimated as 4.55 for cattle manure [23]. The syngas is passed through a two-stage cyclone system to separate the solids (biochar) from the product gas. The beef cattle manure properties are shown in Table 2 (moisture content of 13 wt %). Table 7 shows the results of the syngas and biochar compositions after gasification tests. The syngas composition and LHV for beef cattle are between the ranges of the values reported for pinewood [64].

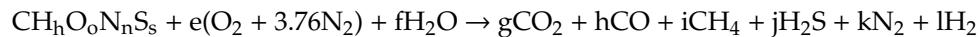
A 10 kW batch fixed-bed counter flow gasifier was used for the gasification of dairy biomass [65]. A mixture of air and steam was used as gasifying agent, and its effects on gas composition, the heating value of gas mixtures, and energy conversion efficiency were studied. Whilst higher HHV of syngas were obtained for low ER values and high S/F ratios, high ER values and S/F ratios favoured the energy conversion efficiency due to a reduction in tar and char production.

Equilibrium calculations have also been used to compare different manure types. A thermodynamic study found that beef cattle manure generated more syngas than the other types (pig manure, dairy cattle manure, layer hen manure and broiler manure) [19]. The calculations assumed the tar content in the syngas as negligible, char consisting of pure carbon, and that 15% of the dry and ash-free animal manure converted into char. The calculations were conducted using a gasification temperature of  $850^\circ\text{C}$  and an ER of 0.3, as shown in Table 7.

When a mixture of air and the steam are used as gasifying agents, the modified equivalence ratio ( $\text{ER}_M$ ) is used, actual oxygen supplied by both air and steam to the stoichiometric oxygen [62]. For complete combustion, the main reaction consists of:



For air and steam gasification, the reaction becomes:



Therefore,  $ER_M$  is defined as:

$$ER_M = \frac{\text{actual oxygen}}{\text{stoichiometric oxygen}} = \frac{2e + f}{2a} \quad (9)$$

The selection of the gasifying agent greatly influences the composition of the syngas. Experiments using oxygen-enriched air have shown that the presence of more oxygen favours carbon dioxide and hydrogen production and the peak temperature within the bed increases. This finding agrees with what is observed with increases in the  $ER$  value [66]. Temperature increases can be controlled by adding steam as a gasifying agent during enriched-air gasification. Enriched-air fluidised bed gasification of dairy cattle manure showed that temperature has the highest influence on syngas composition, LHV and  $\eta_G$ , than  $ER_M$  and oxygen concentration [24].

The adiabatic flame temperature has been reported to vary for different types of biomass, mainly due to differences in their ash and moisture contents. Based on a THERMOLAB spreadsheet, the adiabatic flame temperature was estimated using a curve fit of various agricultural and animal-based biomass fuels with varying moisture (0–45%) and ash (0–40%) contents, and assuming equilibrium concentrations [67]:

$$T = 2010 - 1.8864[\%MC] + 5.0571[\%ash] - 0.3089[\%MC][\%ash] - 0.1802[\%MC]^2 - 0.1076[\%ash]^2 \quad (10)$$

where  $T$  is the temperature in °C,  $\%MC$  is the moisture content in wt %, and  $\%ash$  is in wt %.

#### 4.2.3. Hydrothermal Carbonisation

Hydrothermal carbonisation (HTC) involves heating in a water-environment at temperatures of 350–550 K and pressures of 2–10 MPa, and produces an aqueous liquid fraction containing water-soluble organic compounds called AHL (aqueous HTC liquids), and char which is called hydrochar. HTC benefits from not needing drying as a pre-treatment step but it requires the separation of the hydrochar from the process water [68]. In addition, the hydrochar shows a higher heating value, higher energy yield, and lower ash content than pyrolytic char produced by swine manure. Therefore, HTC is considered as a more effective approach in carbonising animal manure for solid biofuel compared to slow pyrolysis [69].

Studies of HTC of dairy manure to analyse optimal conditions to preserve inorganic nutrients showed that the solid product required a manure/water ratio of 20/200 g/mL at 240 °C and the liquid product 20/200 g/mL at 150 °C. The liquid product contained phosphorus (P) mainly as  $\text{PO}_4^{3-}$ , and most of the potassium (K), which makes HTC a promising technology for the conversion of dairy manure as inorganic fertiliser [70].

#### 4.2.4. Hydrothermal Liquefaction

Hydrothermal liquefaction (HTL) is an emerging technology for energy and chemical production from wet biomasses such as cattle manures by directly liquefying manure into bio-oil without the need for a drying step. HTL operates at temperatures of 200 °C–350 °C and pressures of 4–22 MPa. HTL benefits from simultaneously treating and sterilising waste and deactivating antibiotic-resistant genes in manure. However, the heavy metals concentrate in the solid residue after HTL, which pose environmental concerns [71].

#### 4.2.5. Fuel Production from Cattle Manure

Supercritical water gasification (SCWG) of biomass also does not require drying biomass a priori, which in turn saves energy and time. SCWG involves adjusting the temperature or pressure to change the chemical reaction and the kinetics, which in turn produces compound products in the desired concentrations. SCWG can achieve high solid conversion (more than 99%) and a high concentration of H<sub>2</sub> (up 50%) [72]. SCWG of liquefied cattle manure has shown potential for hydrogen production since the major products are H<sub>2</sub> and CO<sub>2</sub> [73].

#### 4.2.6. Enzymatic Fermentation into Ethanol

Manure falls into this category owing to its relatively high (up to 50%) fibre content. As the major resource component of manure is fibre, converting fibre to biochemicals via a sugar platform provides an approach for this new level of manure utilisation. This process involves hydrolysis of fibre components (cellulose and hemicellulose) into simple sugars, which can be converted to fuel ethanol or other chemicals via chemical or biological processes [74]. Dilute sulphuric acid pretreatment and enzyme hydrolysis is a better approach with total sugar conversions approaching 79%. Fermentation trials with ensuing C6 hydrolysates validated the practicality of converting feedlot cattle manure into ethanol (70% efficiency). With further developments (i.e., fermentation of C5 sugars), this process could deliver greater yields, reinforcing its potential as a biofuel feedstock [75].

#### 4.3. Thermochemical Versus Biological Treatment

Biological treatment, such as composting and vermicomposting, offers elimination of pathogens and odours in manures. In addition, vermicomposting earthworms decrease heavy metal levels by accumulation in non-toxic forms and decreasing their bioavailability through physiological metabolism. However, earthworms after a long stabilisation period may act as a mediator of heavy metal transfer to the higher food chain [43]. For anaerobic digestion operation at thermophilic conditions (>45 °C) can enhance higher solubility of organic compounds, higher chemical and biochemical reaction rates, higher pathogen deactivation and less odour [51].

Thermochemical conversion also offers elimination of odours and pathogens from animal manure with high processing efficiency, reduced waste stream volume, as well as high value-added products, such as biochar, bio-oil and/or syngas. In addition, heavy metals can be trapped in the char produced or in the bed of fluidised bed pyrolysers or gasifiers. This is favoured when additives such as activated carbon, zeolite or calcium oxide are added to increase the capture ability [76].

Pyrolysis and gasification of cattle manure yield char and syngas, respectively, comparable to lignocellulosic biomass. In contrast, anaerobic digestion of cattle manure requires co-processing with lignocellulosic biomass residues to counter to the low and imbalance C/N ratio in animal manures and improve the performance [51].

### 5. Environment and Sustainability

#### 5.1. Contribution to the Energy and Climate Targets

Our need to comply with international targets to tackle climate change should include the increased use of renewable sources. The UK is expected to source 15% of all energy from renewable sources by 2020 under the EU Renewable Energy Directive and reduce carbon emissions (the Climate Change Act 2008) by at least 80% by 2050 compared to 1990 levels. In 2016, 38 GW (87,146 GWh) was reported as installed electricity capacity from renewable sources, with 4 GW from solid biomass and 1.7 GW from biogas. This represented UK GHG emission savings of 41 MtCO<sub>2</sub>e due to renewable electricity [77]. The growth of renewables has depended on the extent of government support. For example, the UK government has set up a number of measures to encourage the generation of energy from renewable sources, such as Renewables Obligation, Feed-in tariff, and Renewable Heat Incentive. Manure conversion into syngas or biogas can receive in the UK support for electricity use through Feed-in



Tariff, which provides a guaranteed price for 10–25 years to small-scale electricity plants of up to 5 MW and receive additional support by Renewables Obligation Certificates, or receive support for heat use under the Renewable Heat Incentive. For plants over 5 MW, Contracts for Difference (CfD) can be in place based on an agreed ‘strike price’, where the difference between market price and ‘strike price’ is paid back to the renewable generator if positive or the CfD Counterparty if negative. In Germany, the Feed-in tariff is only applicable to plants of up to 100 kW for over a period of 20 years, and a market premium for plants with an installed capacity of over 100 kW for electricity sold calculated each month [78]. Since the announcement of the withdrawal of the United States from the Paris Agreement, 23 states have joined the United States Climate Alliance and committed to reducing GHG emissions by at least 26–28% below 2005 levels by 2025. The initiative has set up the Green Bank which finances commercially viable and proven clean energy technologies that face barriers to attracting capital investment [79].

### 5.2. Sustainability Matters

Slurries and solid cattle manure spread directly onto land to provide nutrients to soils can cause water and air pollution. These concerns have promoted better manure management practices, but they differ by farm preferences and/or country. Different management practices generate manure with different physicochemical characteristics, which allow the exploitation of a range of technologies to reduce odours and/or volume, or energy generation. Current practices have focused on mechanical separation and biological treatment. Nonetheless, thermochemical conversion processes such as pyrolysis and gasification have the potential to generate bio-oils, heat and/or power. The final solid residue can be then utilised as fertiliser.

Studies on dairy manure management practices found that manure processing, such as anaerobic digestion, contributes to reducing GHG emissions. In contrast, storing liquid manure for long periods without processing contributed the most to GHG emissions, which is more common in large farms than small farms, which mostly handle solid manure and land-apply manure daily. Therefore, GHG emissions can vary between 2.2 to 12 tCO<sub>2</sub>e per ton of manure from collection, 0.2 to 2.4 tCO<sub>2</sub>e from transportation, 16 to 84 tCO<sub>2</sub>e from storage, and 16 to 33.5 tCO<sub>2</sub>e from land-application [80]. Therefore, the big task of reducing emissions, when currently mass-production of meat and milk in some regions by large farms generates a gigantic amount of manure, is quite challenging without decreasing the number of animals raised.

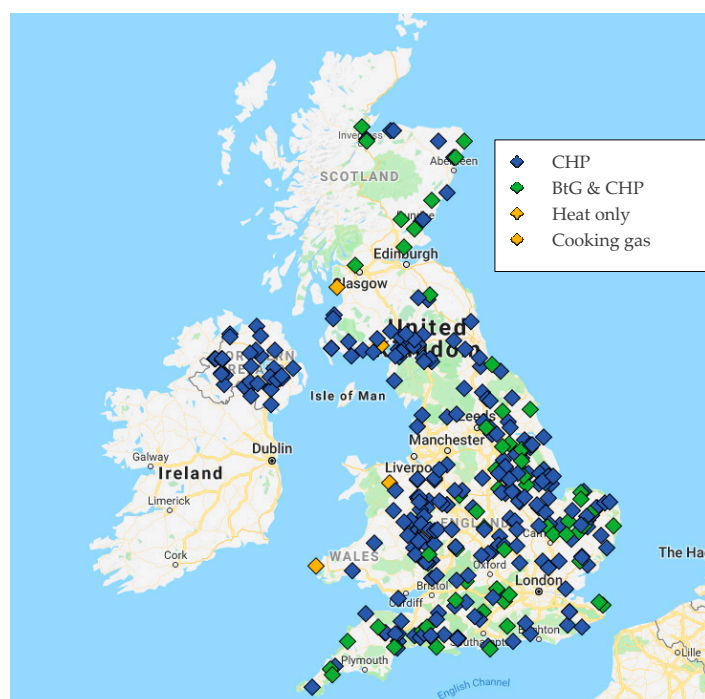
### 5.3. Future Prospects

The use of upgraded biogas to higher methane content (>95%), often called biomethane, is growing as a result of support schemes for applications in transportation or injection into the gas grid. Scarlat, Dallemand [81] present an in-depth analysis of the biogas market and trends in Europe and report that Europe is the world’s leading producer of biomethane as a vehicle fuel with 160 million m<sup>3</sup> used for filling stations and for injection into the natural gas grid with a capacity of 1.5 million m<sup>3</sup> in 2015. According to the European Biogas Association, there are 17,358 biogas plants in Europe with a total installed capacity of 8.7 GW<sub>e</sub> in 2015, and 367 biomethane AD plants with a total upgrading capacity of 310,000 m<sup>3</sup>/h of raw biogas in 2014 [82].

Figure 2 shows up-to-date data of anaerobic digestion plants, 473 in total, operating in the UK using agricultural and waste feedstock. Sixty-two use cattle manure, cattle slurry or a mixture with other agriculture waste making use of 723 kt/y, mostly for combined heat and power (CHP), with capacities ranging from 3 to 1170 kW<sub>e</sub> [83].

Based on the final use of the upgraded biomass, biomethane contains 97–99% methane and 1–3% CO<sub>2</sub>. For pipeline injection, typical specifications indicate content of CO<sub>2</sub> of less than 3%, and as vehicle fuel a combined CO<sub>2</sub>-N<sub>2</sub> content of 1.5–4.5%. Biogas upgrading technologies include water scrubbing which can achieve a composition of >97% CH<sub>4</sub> and simultaneous H<sub>2</sub>S removal, chemical absorption/scrubbing >99% CH<sub>4</sub> with very low CH<sub>4</sub> losses (<0.1%), pressure swing adsorption (PSA)

95–98% CH<sub>4</sub>, and membranes >96% CH<sub>4</sub> [84]. Alternatively, cryogenic/low-temperature upgrading technologies can be used with 90–98% CH<sub>4</sub> with CO<sub>2</sub> and CH<sub>4</sub> in high purity, where the purified gas is obtained directly at low temperatures to readily produce liquid biomethane (LBM) [46]. The selection of the biogas upgrading technologies and their technological improvement is key for the reduction of their energy intensity and making biomethane more attractive to substitute fossil fuels for heating and transportation. Biomethane can be delivered through the existing natural gas pipeline network or supplied by tankers as liquefied natural gas (bio-LNG) for fuelling heavy-duty vehicles [81]. In the UK, the company Gasrec [85] is already operating fuelling stations for LNG and bio-LNG for heavy-good vehicles and expanding to cover vehicles of up to 460 hp. However, the infrastructure for biomethane is scarce in the UK with only around 15 fuelling stations in contrast to around 800 in Germany [83]. This shows the need for support schemes to enable the rapid growth of biogas and biomethane in the transport sector.



**Figure 2.** UK map showing the location of anaerobic digestion plants including their end-use. CHP (combined heat and power), BtG (biomethane to grid). Reproduced with permission from [83]. Copyright NNFCC, 2019.

## 6. Conclusions

Since direct spread onto the land of cattle manure is an unacceptable management practice, biological or thermochemical conversion technologies are needed. Composting and vermicomposting are limited to the elimination of pathogens and odours in manures. In contrast, anaerobic digestion and thermochemical conversion produce valuable gaseous and solid products. However, anaerobic digestion of cattle manure needs co-processing with lignocellulosic biomass residues in order to achieve the C/N ratio needed in the process. Thermochemical conversion overcomes this limitation along with the capture of heavy metals within the char produced. Therefore, the selection of cattle manure management technologies can potentially offer the simultaneous disposal of the waste, reduction of pollutants in water and air, and production of valuable products, such as syngas and biogas. In addition, upgraded biogas or biomethane are of growing interest in the transport sector or for direct injection to the natural gas grid, which could aid to achieve a reduction of GHG emissions.

**Funding:** This research received no external funding.

**Conflicts of Interest:** The author declares no conflicts of interest.

## References

- DEFRA. *Farming Statistics Provisional Crop Areas, Yields and Livestock Populations. At June 2016—United Kingdom*; F.R.A. Department for Environment: London, UK, 2016.
- USDA. *Cattle Inventory*; U.S.D.O. National Agricultural Statistics Service (NASS): Washington, DC, USA, 2019.
- FAOSTAT. *Live Animals—Cattle*; FAOSTAT Nations: Rome, Italy, 2018.
- Carlin, N.T.; Annamalai, K.; Harman, W.L.; Sweeten, J.M. The economics of reburning with cattle manure-based biomass in existing coal-fired power plants for NO<sub>x</sub> and CO<sub>2</sub> emissions control. *Biomass Bioenergy* **2009**, *33*, 1139–1157.
- Smith, K.A.; Williams, A.G. Production and management of cattle manure in the UK and implications for land application practice. *Soil Manag.* **2016**, *32*, 73–82. [[CrossRef](#)]
- Chambers, B.; Nicholson, N.; Smith, K.; Pain, B.; Cumby, T.; Scotford, I. *Making Better Use of Livestock Manures on Arable Land*, 2nd ed.; Ministry of Agriculture, Fisheries and Food: London, UK, 2001.
- DEFRA. *Emissions of Air Pollutants in the UK, 1970 to 2017*; F.R.A. Department for Environment: London, UK, 2019.
- Zhou, D.-M.; Hao, X.Z.; Wang, Y.J.; Dong, Y.H.; Cang, L. Copper and Zn uptake by radish and pakchoi as affected by application of livestock and poultry manures. *Chemosphere* **2005**, *59*, 167–175.
- Technology Focus. An alternative manure treatment technology. *Filtr. Sep.* **2014**, *51*, 44–45.
- De Mendonça Costa, M.S.S.; Cestonaro, T.; de Mendonça Costa, L.A.; Rozatti, M.A.T.; Carneiro, L.J.; Pereira, D.C.; Lorin, H.E.F. Improving the nutrient content of sheep bedding compost by adding cattle manure. *J. Clean. Prod.* **2015**, *86*, 9–14. [[CrossRef](#)]
- Bernal, M.P.; Albuquerque, J.A.; Moral, R. Composting of animal manures and chemical criteria for compost maturity assessment. A review. *Bioresour. Technol.* **2009**, *100*, 5444–5453. [[PubMed](#)]
- Hepperly, P.; Lotter, D.; Ulsh, C.Z.; Seidel, R.; Reider, C. Compost, manure and synthetic fertilizer influences crop yields, soil properties, nitrate leaching and crop nutrient content. *Compost Sci. Util.* **2009**, *17*, 117–126. [[CrossRef](#)]
- Schlegel, A.J.; Assefa, Y.; Bond, H.D.; Wetter, S.M.; Stone, L.R. Corn response to long-term applications of cattle manure, swine effluent, and inorganic nitrogen fertilizer. *Agron. J.* **2015**, *107*, 1701–1710. [[CrossRef](#)]
- Leclerc, A.; Laurent, A. Framework for estimating toxic releases from the application of manure on agricultural soil: National release inventories for heavy metals in 2000–2014. *Sci. Total Environ.* **2017**, *590–591*, 452–460. [[CrossRef](#)]
- Brown, P.; Broomfield, M.; Cardenas, L.; Choudrie, S.; Kilroy, E.; Jones, L.; MacCarthy, J.; Passant, N.; Thistlethwaite, G.; Thomson, A.; et al. *UK Greenhouse Gas Inventory, 1990 to 2016*; Annual Report for Submission under the Framework Convention on Climate Change; E.I.S. Department for Business: London, UK, 2018.
- Brown, P.; Broomfield, M.; Cardenas, L.; Choudrie, S.; Kilroy, E.; Jones, L.; Passant, N.; Thomson, A.; Wakeling, D. *UK Greenhouse Gas Inventory, 1990 to 2015*; Annual Report for submission under the Framework Convention on Climate Change; Department for Business, Energy and Industrial Strategy: London, UK, 2017.
- Myhre, G.; Shindell, D.; Bréon, F.M.; Collins, W.; Fuglestad, J.; Huang, J.; Koch, J.-F.; Lamarque, D.; Lee, B.; Mendoza, T. Anthropogenic and natural radiative forcing. In *Climate Change 2013: The Physical Science Basis. Contribution of Working Group I to the Fifth Assessment Report of the Intergovernmental Panel on Climate Change*; Stocker, T.F., Qin, D., Plattner, G.-K., Tignor, M.M.B., Allen, S.K., Boschung, J., Nauels, A., Xia, Y., Bex, V., Midgley, P.M., Eds.; Cambridge University Press: Cambridge, UK, 2013.
- USDA. *Dairy 2007: Facility Characteristics and Cow Comfort on U.S. Dairy Operations*; USDA: Washington, DC, USA, 2010.
- Shen, X.; Huang, G.; Yang, Z.; Han, L. Compositional characteristics and energy potential of Chinese animal manure by type and as a whole. *Appl. Energy* **2015**, *160*, 108–119.
- Phyllis2. *Database for Biomass and Waste*; Energy Research Centre of The Netherlands: Petten, The Netherlands, 2012.
- Wang, L.; Shahbazi, A.; Hanna, M.A. Characterization of corn stover, distiller grains and cattle manure for thermochemical conversion. *Biomass Bioenergy* **2011**, *35*, 171–178. [[CrossRef](#)]

22. Sweeten, J.M.; Annamalai, K.; Thien, B.; McDonald, L.A. Co-firing of coal and cattle feedlot biomass (FB) fuels. Part I. Feedlot biomass (cattle manure) fuel quality and characteristics. *Fuel* **2003**, *82*, 1167–1182.
23. Maglinao, A.L., Jr.; Capareda, S.C.; Nam, H. Fluidized bed gasification of high tonnage sorghum, cotton gin trash and beef cattle manure: Evaluation of synthesis gas production. *Energy Conv. Manag.* **2015**, *105*, 578–587. [[CrossRef](#)]
24. Nam, H.; Maglinao, A.L., Jr.; Capareda, S.C.; Rodriguez-Alejandro, D.A. Enriched-air fluidized bed gasification using bench and pilot scale reactors of dairy manure with sand bedding based on response surface methods. *Energy* **2016**, *95*, 187–199. [[CrossRef](#)]
25. Brugger, D.; Windisch, W.M. Environmental responsibilities of livestock feeding using trace mineral supplements. *Anim. Nutr.* **2015**, *1*, 113–118. [[CrossRef](#)] [[PubMed](#)]
26. Nicholson, F.A.; Chambers, B.J.; Williams, J.R.; Unwin, R.J. Heavy metal contents of livestock feeds and animal manures in England and Wales. *Bioresour. Technol.* **1999**, *70*, 23–31. [[CrossRef](#)]
27. WRAP. *Specification for Composted Materials—BSI\_PASS 100*; The Waste & Resources Action Programme (WRAP): Banbury, UK, 2011.
28. Yang, X.; Li, Q.; Tang, Z.; Zhang, W.; Yu, G.; Shen, Q.; Zhao, F.J. Heavy metal concentrations and arsenic speciation in animal manure composts in China. *Waste Manag.* **2017**, *64*, 333–339. [[CrossRef](#)]
29. Misselbrook, T.H.; Smith, K.A.; Johnson, R.A.; Paina, B.F. Slurry application techniques to reduce ammonia emissions: Results of some UK Field-scale experiments. *Biosyst. Eng.* **2002**, *81*, 313–321. [[CrossRef](#)]
30. Green, M.J.; Leach, K.A.; Breen, J.E.; Ohnstad, I.; Tuer, S.; Archer, S.C.; Bradley, A.J. Recycled manure solids as bedding for dairy cattle: A scoping study. *Cattle Pract.* **2014**, *22*, 207–214.
31. Bradley, A. *Risks, Benefits and Optimal Management of Recycled Manure Solids for use as Bedding for Dairy Cattle*; AHDB Dairy: Kenilworth, UK, 2015.
32. Cao, H.; Xin, Y.; Yuan, Q. Prediction of biochar yield from cattle manure pyrolysis via least squares support vector machine intelligent approach. *Bioresour. Technol.* **2016**, *202*, 158–164. [[CrossRef](#)]
33. EPA. *Wastewater Technology Fact Sheet—Anaerobic Lagoons*; U.S.E.P. Agency: Washington, DC, USA, 2012.
34. BIOWiSH. BIOWiSH Technologies. Available online: <https://int.biowishtechnologies.com/> (accessed on 9 February 2019).
35. LWR. Livestock Water Recycling. Available online: <http://www.livestockwaterrecycling.com/> (accessed on 9 February 2019).
36. Allance. Allance Fertilizer Machinery. Available online: <http://www.fertilizer-machine.net/> (accessed on 9 March 2019).
37. DariTech. Beddingmaster. Available online: <http://www.daritech.com/products.html> (accessed on 9 March 2019).
38. McLanahan. Sand-Manure Separators (SMS). Available online: <http://mclanahan.com/products/sand-manure-separators-sms/> (accessed on 20 March 2019).
39. GEA. Manure Separators. Available online: <http://www.gea.com/en/productgroups/farm-equipment/manure-separators/index.jsp> (accessed on 20 March 2019).
40. HoST. Microferm® and Macroferm®: Manure Digestion. Available online: [http://www.host.nl/en/biogas-plants/manure-digestion-microferm/?gclid=EAIaIQobChMI-ajpm77y1AIVFBbTChInOAluEAAAYBCAAEgIJm\\_D\\_BwE](http://www.host.nl/en/biogas-plants/manure-digestion-microferm/?gclid=EAIaIQobChMI-ajpm77y1AIVFBbTChInOAluEAAAYBCAAEgIJm_D_BwE) (accessed on 20 March 2019).
41. DairyEnergy. Micro Anaerobic Biogas Systems Designed To Run On Only Dairy Slurry. Dairy Energy; 2017. Available online: <https://www.dairyenergy.co.uk/> (accessed on 20 March 2019).
42. Lazcano, C.; Gómez-Brandón, M.; Domínguez, J. Comparison of the effectiveness of composting and vermicomposting for the biological stabilization of cattle manure. *Chemosphere* **2008**, *72*, 1013–1019. [[CrossRef](#)]
43. Eghball, B.; Power, J.F.; Gilley, J.E.; Doran, J.W. Nutrient, carbon, and mass loss during composting of beef cattle feedlot manure. *J. Environ. Qual.* **1997**, *26*, 189–193. [[CrossRef](#)]
44. Domínguez, J.; Edwards, C.A.; Subler, S. A comparison of composting and vermicomposting. *Biocycle* **1997**, *4*, 57–59.
45. Swati, A.; Hait, S. Fate and bioavailability of heavy metals during vermicomposting of various organic wastes—A review. *Process Saf. Environ. Prot.* **2017**, *109*, 30–45. [[CrossRef](#)]
46. Pellegrini, L.A.; De Guido, G.; Langé, S. Biogas to liquefied biomethane via cryogenic upgrading technologies. *Renew. Energy* **2018**, *124*, 75–83. [[CrossRef](#)]
47. Xavier, C.A.; Moset, V.; Wahid, R.; Møller, H.B. The efficiency of shredded and briquetted wheat straw in anaerobic co-digestion with dairy cattle manure. *Biosyst. Eng.* **2015**, *139*, 16–24. [[CrossRef](#)]



48. Henze, M.; van Loosdrecht, M.C.; Ekama, G.A.; Brdjanovic, D. *Biological Wastewater Treatment—Principles, Modelling and Design*; IWA Publishing: London, UK, 2008.
49. Luque, R.; Campelo, J.; Clark, J. *Handbook of Biofuels Production—Processes and Technologies*; Woodhead Publishing: Cambridge, UK, 2011.
50. Li, Y.; Park, S.Y.; Zhu, J. Solid-state anaerobic digestion for methane production from organic waste. *Renew. Sustain. Energy Rev.* **2011**, *15*, 821–826. [[CrossRef](#)]
51. Neshat, S.A.; Mohammadi, M.; Najafpour, G.D.; Lahijani, P. Anaerobic co-digestion of animal manures and lignocellulosic residues as a potent approach for sustainable biogas production. *Renew. Sustain. Energy Rev.* **2017**, *79*, 308–322. [[CrossRef](#)]
52. Lehtomäki, A.; Huttunen, S.; Rintala, J.A. Laboratory investigations on co-digestion of energy crops and crop residues with cow manure for methane production: Effect of crop to manure ratio. *Resour. Conserv. Recycl.* **2007**, *51*, 591–609. [[CrossRef](#)]
53. Kalamaras, S.D.; Kotsopoulos, T.A. Anaerobic co-digestion of cattle manure and alternative crops for the substitution of maize in South Europe. *Bioresour. Technol.* **2014**, *172*, 68–75. [[CrossRef](#)]
54. Ledda, C.; Schievano, A.; Scaglia, B.; Rossoni, M.; Fernández, F.G.A.; Adani, F. Integration of microalgae production with anaerobic digestion of dairy cattle manure: An overall mass and energy balance of the process. *J. Clean. Prod.* **2016**, *112*, 103–112. [[CrossRef](#)]
55. Uzoma, K.C.; Inoue, M.; Andry, H.; Fujimaki, H.; Zahoor, A.; Nishihara, E. Effect of cow manure biochar on maize productivity under sandy soil condition. *Soil Manag.* **2011**, *27*, 205–212. [[CrossRef](#)]
56. Cao, X.; Harris, W. Properties of dairy-manure-derived biochar pertinent to its potential use in remediation. *Bioresour. Technol.* **2010**, *101*, 5222–5228. [[CrossRef](#)] [[PubMed](#)]
57. Jeong, Y.W.; Choi, S.K.; Choi, Y.S.; Kim, S.J. Production of biocrude-oil from swine manure by fast pyrolysis and analysis of its characteristics. *Renew. Energy* **2015**, *79*, 14–19. [[CrossRef](#)]
58. Yuan, X.; He, T.; Cao, H.; Yuan, Q. Cattle manure pyrolysis process: Kinetic and thermodynamic analysis with isoconversional methods. *Renew. Energy* **2017**, *107*, 489–496. [[CrossRef](#)]
59. McKendry, P. Energy production from biomass (part 2): Conversion technologies. *Bioresour. Technol.* **2002**, *83*, 47–54. [[CrossRef](#)]
60. Zhu, X.; Venderbosch, R. A correlation between stoichiometrical ratio of fuel and its higher heating value. *Fuel* **2005**, *84*, 1007–1010. [[CrossRef](#)]
61. Mathieu, P.; Dubuisson, R. Performance analysis of a biomass gasifier. *Energy Conv. Manag.* **2002**, *43*, 1291–1299. [[CrossRef](#)]
62. Gordillo, G.; Annamalai, K.; Carlin, N. Adiabatic fixed-bed gasification of coal, dairy biomass, and feedlot biomass using an air–steam mixture as an oxidizing agent. *Renew. Energy* **2009**, *34*, 2789–2797. [[CrossRef](#)]
63. Lv, P.M.; Xiong, Z.H.; Chang, J.; Wu, C.Z.; Chen, Y.; Zhu, J.X. An experimental study on biomass air–steam gasification in a fluidized bed. *Bioresour. Technol.* **2004**, *95*, 95–101. [[CrossRef](#)]
64. Gil, J.; Corella, J.; Aznar, M.P.; Caballero, M.A. Biomass gasification in atmospheric and bubbling fluidized bed: Effect of the type of gasifying agent on the product distribution. *Biomass Bioenergy* **1999**, *17*, 389–403. [[CrossRef](#)]
65. Gordillo, G.; Annamalai, K. Adiabatic fixed bed gasification of dairy biomass with air and steam. *Fuel* **2010**, *89*, 384–391. [[CrossRef](#)]
66. Thanapal, S.S.; Annamalai, K.; Sweeten, J.M.; Gordillo, G. Fixed bed gasification of dairy biomass with enriched air mixture. *Appl. Energy* **2012**, *97*, 525–531. [[CrossRef](#)]
67. Annamalai, K.; Priyadarsan, S.; Arumugam, S.; Sweeten, J.M. Energy conversion: Principles for coal, animal waste, and biomass fuels. In *Encyclopedia of Energy Engineering and Technology*, 2nd ed.; Capenhart, B.L., Ed.; Taylor & Francis: Abingdon, UK, 2008; pp. 476–497.
68. Pecchi, M.; Baratieri, M. Coupling anaerobic digestion with gasification, pyrolysis or hydrothermal carbonization: A review. *Renew. Sustain. Energy Rev.* **2019**, *105*, 462–475. [[CrossRef](#)]
69. Zhou, S.; Liang, H.; Han, L.; Huang, G.; Yang, Z. The influence of manure feedstock, slow pyrolysis, and hydrothermal temperature on manure thermochemical and combustion properties. *Waste Manag.* **2019**, *88*, 85–95. [[CrossRef](#)]
70. Wu, K.; Zhang, X.; Yuan, Q. Effects of process parameters on the distribution characteristics of inorganic nutrients from hydrothermal carbonization of cattle manure. *J. Environ. Manag.* **2018**, *209*, 328–335. [[CrossRef](#)] [[PubMed](#)]

71. Li, H.; Lu, J.; Zhang, Y.; Liu, Z. Hydrothermal liquefaction of typical livestock manures in China: Biocrude oil production and migration of heavy metals. *J. Anal. Appl. Pyrolysis* **2018**, *135*, 133–140. [CrossRef]
72. Lachos-Perez, D.; Juliana, P.M.; Torres-Mayanga, P.; Forster-Carneiro, T.; Meireles, M. Supercritical water gasification of biomass for hydrogen production: Variable of the process. *Food Public Health* **2015**, *5*, 92–101.
73. Tushar, M.S.H.K.; Dutta, A.; Xu, C. Catalytic supercritical gasification of biocrude from hydrothermal liquefaction of cattle manure. *Appl. Catal. B Environ.* **2016**, *189*, 119–132. [CrossRef]
74. Chen, S.; Wen, Z.; Liao, W.; Liu, C.; Kincaid, R.L.; Harrison, J.; Elliott, D.C.; Brown, D.; Stevens, D.J. Studies into Using Manure in a Biorefinery Concept. In *Twenty-Sixth Symposium on Biotechnology for Fuels and Chemicals*; Davison, B.H., Ed.; Humana Press: New York, NY, USA, 2005.
75. Vancov, T.; Schneider, R.C.S.; Palmer, J.; McIntosh, S.; Stuetz, R. Potential use of feedlot cattle manure for bioethanol production. *Bioresour. Technol.* **2015**, *183*, 120–128. [CrossRef]
76. Lin, C.-L.; Wu, M.-H.; Weng, W.-C. Effect of the type of bed material in two-stage fluidized bed gasification reactors on hydrogen gas synthesis and heavy metal distribution. *Int. J. Hydrog. Energy* **2019**, *44*, 5633–5639. [CrossRef]
77. European Commission. Fourth Progress Report on the Promotion and use of Energy From Renewable Sources for the United Kingdom 2016. Available online: <https://ec.europa.eu/energy/en/topics/renewable-energy/progress-reports> (accessed on 20 March 2019).
78. European Commission. Renewable Energy Policy Database and Support Legal Sources on Renewable Energy—Legal Sources on Renewable Energy 2014. Available online: <http://www.res-legal.eu/home/> (accessed on 20 March 2019).
79. Alliance, U.S.C. United States Climate Alliance. Available online: <https://www.usclimatealliance.org/> (accessed on 20 March 2019).
80. Aguirre-Villegas, H.A.; Larson, R.A. Evaluating greenhouse gas emissions from dairy manure management practices using survey data and lifecycle tools. *J. Clean. Prod.* **2017**, *143*, 169–179. [CrossRef]
81. Scarlat, N.; Dallemand, J.-F.; Fahl, F. Biogas: Developments and perspectives in Europe. *Renew. Energy* **2018**, *129*, 457–472. [CrossRef]
82. EBA. Biogas and Biomethane 2015. Available online: <http://european-biogas.eu/publications-homepage/biogas-and-biomethane/> (accessed on 20 March 2019).
83. Biogas. The Official Information Portal on Anaerobic Digestion. Available online: <http://www.biogas-info.co.uk/about/biogas/> (accessed on 20 March 2019).
84. Ryckebosch, E.; Drouillon, M.; Vervaeren, H. Techniques for transformation of biogas to biomethane. *Biomass Bioenergy* **2011**, *35*, 1633–1645. [CrossRef]
85. Gasrec. Gasrec Ltd. Available online: <https://www.gasrec.co.uk/> (accessed on 20 March 2019).



© 2019 by the author. Licensee MDPI, Basel, Switzerland. This article is an open access article distributed under the terms and conditions of the Creative Commons Attribution (CC BY) license (<http://creativecommons.org/licenses/by/4.0/>).